THE ROLE OF BIOLOGICAL VOLATILIZATION IN SELENIUM REMOVAL BY THE IMPERIAL CONSTRUCTED WETLANDS, IMPERIAL, CA

A Thesis

Presented to the

Faculty of

San Diego State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Public Health

with a concentration in

Environmental Health

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by

Marcelo do Vale Braga

Spring 2011

SAN DIEGO STATE UNIVERSITY

The Undersigned Faculty Committee Approves the

Thesis of Marcelo do Vale Braga:

The Role of Biological Volatilization in Selenium Removal by The Imperial

Constructed Wetlands, Imperial, CA

Richard M. Gersberg, Chair
Graduate School of Public Health

Eunha Hoh
Graduate School of Public Health

Paul Ganster
Department of History

12. 22. 2010

Approval Date

DEDICATION

This thesis is dedicated to my wife, who has provided me with invaluable guidance and support throughout the entire thesis writing process and has instilled the confidence in me that I really can achieve anything with a strong work ethic and persistence. In addition, I'd like to dedicate this thesis to my parents, who sacrificed tremendously in order to provide me with quality education and love throughout my entire life.

ABSTRACT OF THE THESIS

The Role of Biological Volatilization in Selenium Removal by The Imperial Constructed Wetlands, Imperial, CA
by
Marcelo do Vale Braga
Master of Public Health with a concentration in Environmental Health
San Diego State University, 2011

Management of agricultural drainage water contaminated with selenium is one of the most important environmental issues in California. A constructed wetland is an attractive water treatment option due to its low cost and minimal maintenance. The removal of volatile selenium from wetlands is called phytoremediation and is important for its potential in cleaning water polluted with selenium. Selenium ecotoxicity is generally encountered in arid or semiarid regions with alkaline and seleniferous soil derived from marine sediments. Selenium is mobilized and transported by irrigation drainage via tile drains and canals to wetlands and other water-bodies, where bioaccumulation of selenium to toxic levels occurs. The primary goal of constructed wetlands is to remove or decrease pollutants from water-bodies. Toxicity to wild life should also be taken in consideration when evaluating efficiency of removal of selenium in these wetlands, as they are crucial in supporting wildlife habitat. The objective of the present study was to quantitatively determine the rate of selenium (Se) removal by biological volatilization in the Imperial constructed wetlands in Imperial Valley, California. Volatile Se was collected continuously using an open flow chamber system throughout a 24 h sampling period at an airflow rate of $0.43 m^3 h^{-1}$ from vegetated and non-vegetated areas of the Imperial constructed wetlands. Volatile Se in the air was trapped using an alkaline peroxide trap solution (30% H_2O_2 and ~0.05 M NaOH). Selenium volatilization was measured in the Imperial wetlands site during the months of May. June, July, September and October of 2010. The chemical form of volatile Se measured was dimethyl selenide. Rates for the most dominant plant species, saltmarsh bulrush, varied during the months that Se volatilization were measured. In May the rates for vegetated sites were 342.8 µg Se m^{-2} day^{-1}; this rate corresponded to a percent removal of 10.4%. In June, July, September and October the rates for vegetated sites were 46.0, 3.2, 2.1 and 0.9 µg Se m^{-2} day^{-1} and for non-vegetated sites were 7.0, 1.1, 0.4 and 0.2 µg Se m^{-2} day^{-1}; these rates correspond to percent removals of 1.4%, 0.1%, 0.06%, 0.03% and 1.6%, 0.3%, 0.1%, 0.04% respectively. Using mean rates that were measured for biological volatilization, we estimated that the Imperial constructed wetlands might have removed as much as 2.4% and 0.5% of the total Se removed from the inflow through Se volatilization for vegetated and non-vegetated sites respectively. This study concluded that biological volatilization as a means of Se removal in constructed wetlands is a significant pathway that should be further evaluated.

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ACKNOWLEDGEMENTS

I thank my thesis chair, Dr. Richard Gersberg, and my other thesis committee members, Dr. Eunha Hoh and Dr. Paul Ganster, for providing me with direction, assistance, and constructive criticism with the writing and data analysis processes for my thesis. In addition, I want to thank Ms. Kayo Watanabe who was responsible for the laboratory portion of this study, and graduate student Ms. Tiffany Butcher for assisting me in the field. I really appreciate all the assistance and support provided to me in order to successfully complete this Masters thesis.

CHAPTER 1

INTRODUCTION

Selenium (Se) contamination of agricultural drainage has become an important issue in the western part of the United States, after accumulation of bioavailable Se to high concentrations in aquatic systems, and failure to recognize selenium as an environmentally hazardous constituent in wastewater resulted in extensive damage and death of numerous fish and aquatic bird species. Selenium has been studied in detail for more than twenty years since selenium poisoning was discovered in fish and waterfowl in the habitats receiving agricultural drainage at the Kesterson Reservoir in the San Joaquin Valley of California in the early 1980s. It has been shown in the Kesterson Reservoir, CA that selenium concentrations between 5 and 10 μg/g in birds' diet have caused adverse health effects such as reproductive impairment, comprised of embryonic mortality and deformity (Lemly & Ohlendorf, 2002; Ohlendorf, Hoffman, Saiki, & Aldrich, 1986). Selenium is an essential nutrient for living organisms; however, the threshold between being essential and toxic is very narrow, particularly for birds and aquatic species (Cai, 2003; USEPA, 1998; Lemly, 1997). Bioaccumulation of selenium up to the toxic levels has been observed in constructed wetlands and other water bodies generally located in arid or semiarid regions with alkaline and seleniferous soil derived from marine sediments via tile drains and canals (U.S. Bureau of Reclamation, 1986). Excessive irrigation, evaporation and agricultural drain can increase the concentration of selenium in the water above the water quality criterion of 5μg/L established by the United States Environmental Protection Agency (USEPA, 2000).

Constructed wetlands are increasingly being used to control agricultural pollution problems resulting from concentrated and intensive farming practices in many regions of the world. This practice has been utilized for over 30 years in both the United States (Brown & Reed, 1994) and Europe (Haberl, Perfler, & Mayer, 1995) and for more than 20 years in North China (Chianfa & Chuncai, 1995). Constructed wetlands have become an excellent alternative in water treatment for industrial, municipal and agricultural wastewater because of their low cost and minimal maintenance (Frankenberger et al., 2004). In addition, constructed wetlands can substantially improve down-gradient water quality by removing pollutants through a variety of physical, chemical and biological process. However, the effectiveness of detoxification mechanisms can be more than offset by toxic hazards created within the wetlands.

The Imperial wetlands is a constructed treatment site adjacent to the New River in Imperial Valley, California, which was implemented to treat agricultural drainwaters, thereby reducing levels of pollutants, and improving the quality of water discharged from the New River into the Salton Sea. Although irrigation water supplied to the Imperial Valley has selenium levels around 2 µg/L (Setmire & Schroeder, 1998), excessive irrigation and evaporation contribute to selenium bioaccumulation, resulting in selenium levels in the range of 6 to 28 µg/L, with average concentrations of selenium at 8 µg/L (Setmire & Schroeder, 1998).

Biogenic volatilization of selenium from soil and plant tissues is an important process for removing selenium from selenium-contaminated aquatic ecosystems (Frankenberger & Karlson, 1994a). Plants and microbes have the ability to take up inorganic forms of Se such as selenate and/or selenite and convert them to less toxic volatile forms consisting primarily of dimethyl selenide (DMSe). DMSe has been shown to be approximately 500 times less toxic than inorganic forms of Se (Lin & Terry, 2003).

Despite the importance of volatilization in the remediation of Se-contaminated agricultural wastewaters, it remains to be further investigated how significant volatilization can be as a pathway of Se removal by constructed wetlands. Previous studies indicated that constructed wetlands could remove up to 30 percent of the dissolved selenium in agricultural drainwaters in the Kesterson Ponds through biological volatilization (Cooke & Bruland, 1987). Johnson, Gersberg, Rigby, and Roy (2009) estimated through mass balance calculations that 17-61% of the selenium was lost through volatilization on the New River Wetlands Project. However, they did not measure volatilization directly as opposed to this study, which measures it directly. Although, there's some published data on the removal of selenium from agricultural drainwaters flowing into the Imperial constructed wetlands in Imperial Valley, California, the efficiency of removal, the fate of selenium and ecotoxicity risk to wildlife at this site is not fully understood.

Relatively few field studies have been made to measure Se volatilization under naturally occurring wetland conditions. Most Se volatilization studies have been conducted in greenhouses and/or laboratories (Doran & Alexander, 1977; Hamdy & Gissel-Nielsen, 1976; Reamer & Zoller, 1980; Zieve & Peterson, 1981, 1985. These research studies have contributed tremendously with valuable information on the microbiology and chemistry of Se volatilization from soils and plants. The experimental conditions of these studies, however, are generally artificial and may not recreate the inherent conditions of natural environments and therefore, can not be extrapolated with confidence to field experiments (Biggar & Jayaweera, 1993).

The goal of the present study is to quantitatively determine the rate of selenium (Se) removal by biological volatilization in the Imperial constructed wetlands in Imperial Valley, California. In addition, this study will provide useful information on the spatial and temporal dynamics of Se volatilization in constructed wetlands, and will also show that Se volatilization through methylation does occur to a significant extent.

Specific outline of study objectives includes:

1. Measure the rate of selenium volatilization in the Imperial constructed wetlands by trapping volatile Se species in chambers incubated in situ for vegetated and non-vegetated sites in the constructed wetlands.
2. Based upon the mass loss via volatilization estimates, determine the quantitative role in removing selenium through volatilization of the Imperial constructed wetlands ecosystem in the Imperial Valley.

CHAPTER 2

LITERATURE REVIEW

SOURCES AND IMPACT OF SELENIUM CONTAMINATION

Selenium is a natural trace element occurring in a number of inorganic forms, such as selenide, selenate, and selenite. It is also found in organic compounds such as dimethyl selenide, selenomethionine and selenocysteine. Natural sources of selenium include certain seleniferous soils, and selenium that has been bioconcentrated by certain plants, while anthropogenic sources of selenium include mining, coal burning, smelting of sulfide ores, petrochemical and other industrial processes. Selenium pollution is a worldwide phenomenon associated with a broad spectrum of human activities ranging from the most basic agricultural practices to the most high-tech industrial activities observed in oil refineries, coal processing plants and other industries that contain high concentrations of selenium leading to significant environmental hazards (Lemly, 1985). Selenium contamination of agricultural drainage is an important environmental issue in the western United States (Bañuelos & Lin, 2006). The ash remaining from burning coal to produce electricity contains as much as 1,250 times the naturally occurring amount of 0.2 µg/g of selenium found in the Earth's crust, which can be leached out of storage piles by rainwater runoffs into aquatic environments (Lemly & Ohlendorf, 2002). In the United States, selenium waste discharges from power plants have eliminated entire populations of reservoir fish (Lemly & Ohlendorf, 2002). Severe reproductive failure in fish and birds are the hallmark features of chronic selenium toxicity in aquatic environments. Investigations of a massive extinction of several fish species in Belews Lake, NC, which received effluent from ash ponds of a coal-fired power plant in the late 1970s was linked to selenium toxicity in the food chain (Cumbie & Van Horn, 1978; Hamilton, 2004; Holland, 1979; Lemly, 1982, 1985; Sorensen & Bauer, 1984). Crude oil contains even higher levels of selenium (500-2200 µg/l) than coal (Lemly & Ohlendorf, 2002); therefore historic and recent major oil spills have contributed enormously to selenium contamination of aquatic environments. Concerns over other pollutants and other industrial chemicals have overshadowed selenium contamination from the oil industry. In soils, selenium most often occurs in soluble forms such as selenate, which are easily leached into rivers by runoff. Industrial manufacturing processes such as coal processing plants and oil refineries have contaminated bodies of water with selenium causing the bioaccumulation of selenium in aquatic systems resulting in damage to wildlife. Selenium contamination of aquatic habitats can take place in urban, suburban, and rural settings. Irrigation drainwaters used for wetland management, contaminated with high concentrations of selenium, culminated in a massive poisoning of thousands of fish and waterfowl at the Kesterson National Wildlife Refuge in the San Joaquin Valley in California (Ohlendorf, Hoffman, et al., 1986), which became one of the most important environmental Se disasters to date.

THE KESTERSON MARSH EPISODE

The Kesterson Marsh episode is one of the most classic cases for illustrating contamination of wetlands. In 1985, accumulation of biovailable Se to high concentrations in aquatic systems was implicated as the cause of adverse effects on health and reproduction of wildlife at the Kesterson National Wildlife Refuge in the San Joaquin Valley (Ohlendorf, Hoffman, et al., 1986). Since this episode, extensive studies in the lab and field have investigated how bioaccumulation of selenium may lead to toxicological impact and change in aquatic communities. These studies have been recognized as one of the “gold standards” of retrospective ecological risk assessment, as discussed by Suter (1993). Initial concerns about selenium were identified when adult birds were found dead in unusually high numbers. Aquatic birds nesting at Kesterson Reservoir were also found to have high rates of embryo deformity and mortality (Ohlendorf, Hoffman, et al., 1986). The Reservoir, which consisted of a series of twelve shallow ponds collectively known as Kesterson Marsh, was used by the San Luis Drain for disposal of subsurface drainage with high concentrations of selenium from agricultural fields in California’s San Joaquin Valley. Preliminary analyses of San Luis Drain water between March 1981 and February 1982 by the U.S. Bureau of Reclamation (USBR) identified several inorganic elements that approached or exceeded harmful concentrations for freshwater life (based on USEPA, 1976) including selenium (106-45 μg/l). Naturally occurring salts and trace elements such as selenium were leached from soils on the west side of the San Joaquin Valley and were carried in return flows that were used for wetland management (Zahm, 1986). It is estimated that selenium bioaccumulated in aquatic food chains and contaminated 500 ha of shallow marshes. Agricultural drainwaters of the San Joaquin Valley had concentrations of dissolved selenium up to 1400 μg/l in the entrance pond and 14 μg/l in the last of the twelve ponds, resulting in accumulation of selenium in the algal mat approaching a level of 13 mg/g dry weight, which is considered to be toxic to aquatic birds (Presser, 1994). Every species coming in contact with these waters, from fish and birds to insects, amphibious, reptiles and mammals, was found to have elevated concentrations of selenium that were proofed to have caused congenital malformation in young water birds which included missing eyes and feet, protruding brains, and grossly deformed legs, wings and beaks (Clark, 1987; Hoffman, Ohlendorf, & Aldrich, 1988; Ohlendorf, Hoffman, et al., 1986; Ohlendorf et al., 1988; Ohlendorf, Lowe, Kelly, & Harvey, 1986; Saiki & Lowe, 1987). Saiki and Lowe (1987) showed that several species of fish were eliminated and a high frequency (30%) of stillbirths occurred in the single remaining specie. Field assessments combined with laboratory studies conducted by the U.S. Fish and Wildlife Services (USFWS) confirmed that irrigation drainage was the cause of this fish and wildlife-poisoning event (Lemly, Finger, & Nelson, 1993). The findings at Kesterson Reservoir were highly publicized generating political and scientific controversy that ultimately resulted in awareness of the risks posed by agricultural irrigation drainage. Kesterson was declared a toxic waste site, taken out of the national wildlife refuge system, and partially buried (Lemly et al., 1993).

SALTON SEA

The Salton Sea is a saline lake located in the Imperial Valley of Southern California. The New Whitewater and Alamo rivers feed the Sea, which also receives agricultural drainage water and sewage effluent from the United States and Mexico (Glenn, Cohen, Morrison, Valdés-Casillas, & Fitzsimmons, 1999). The Sea has a surface area of approximately 376 square miles, being the largest inland water body in California. The Salton Sea supports a recreational fishery and is a major resting stop for migratory waterfowl on the Pacific Flyway.

The Salton Sea is a system of accelerated change due to the lack of a natural outlet and also due to an imbalance between inflow and evaporation that cause the salinity to rise each year (U.S. Bureau of Reclamation, 2007). After having collected agricultural drainage water for almost a century, the Seas' salinity is continuously increasing, and is expected to become a hyper saline water body in the next two decades, too salty to support fish and other elements of the food chain. The average salinity of the Salton Sea is now 50 g/L, 25% saltier than the water of the Pacific Ocean and many species of fish are no longer able to reproduce or survive in this condition. Depending upon inflow rates and its water salinity, the salinity of the Salton Sea is projected to increase at a rate of approximately 0.2 to 0.3 g/L per year, so the salinity of the sea will reach 90 g/L by the year 2100 (M. Matsumoto, University of California at Riverside, Department of Chemical and Environmental Engineering, unpublished data). Currently, total inflows are approximately 1.7×10^9 m^3/yr, containing approximately 3 g/L of salts and approximately 1.4×10^4 tons of nutrients such as nitrogen and phosphorus from fertilizer runoff and sewage effluent, plus varying (depending on the source) levels of selenium and other metals, pesticide residues and other contaminants from Mexico (Glenn et al., 1999). In 1986, the public was strictly advised to limit consumption of fish from the Salton Sea due to high levels of selenium.

One biological hazard linked to the detritus-fish-bird food chain is potential selenium toxicity (Saiki, 1990; Setmire & Schroeder, 1998). The water in the Salton Sea contains relatively low levels of Se (1μg/Kg), however the selenium in the sea has been biomagnified in the food chain to higher levels hazardous to wildlife (Ohlendorf, Hoffman, et al., 1986; Presser, 1994). It was found that 40% of the bird species evaluated in the Imperial Valley utilizing the Salton Sea as a feeding station, had whole-body selenium contents that exceeded the 30 μg/g threshold associated with high biological risk (see Figure 1). Bird mortalities or deformities related to selenium have not been documented from the Salton Sea, although a few studies have postulated that some bird species such as black-necked stilts show reduced reproductive success (Setmire, Wolfe, & Stroud, 1990). Therefore, selenium toxicity in the Salton Sea is more a potential rather than an actual hazard at the present time.

Increasing wastewater inflows from the New River and agricultural runoff have resulted in elevated bacterial levels and large algal blooms in the Salton Sea. The combined effects of increasing temperature, salinity and bacterial levels have caused massive fish kills and bird die-offs in recent years (1992, 1994, 1996, 1999, 2006, 2008), which has led to a perception that this ecosystem is in trouble and in need of an initiative to restore the Salton Sea.

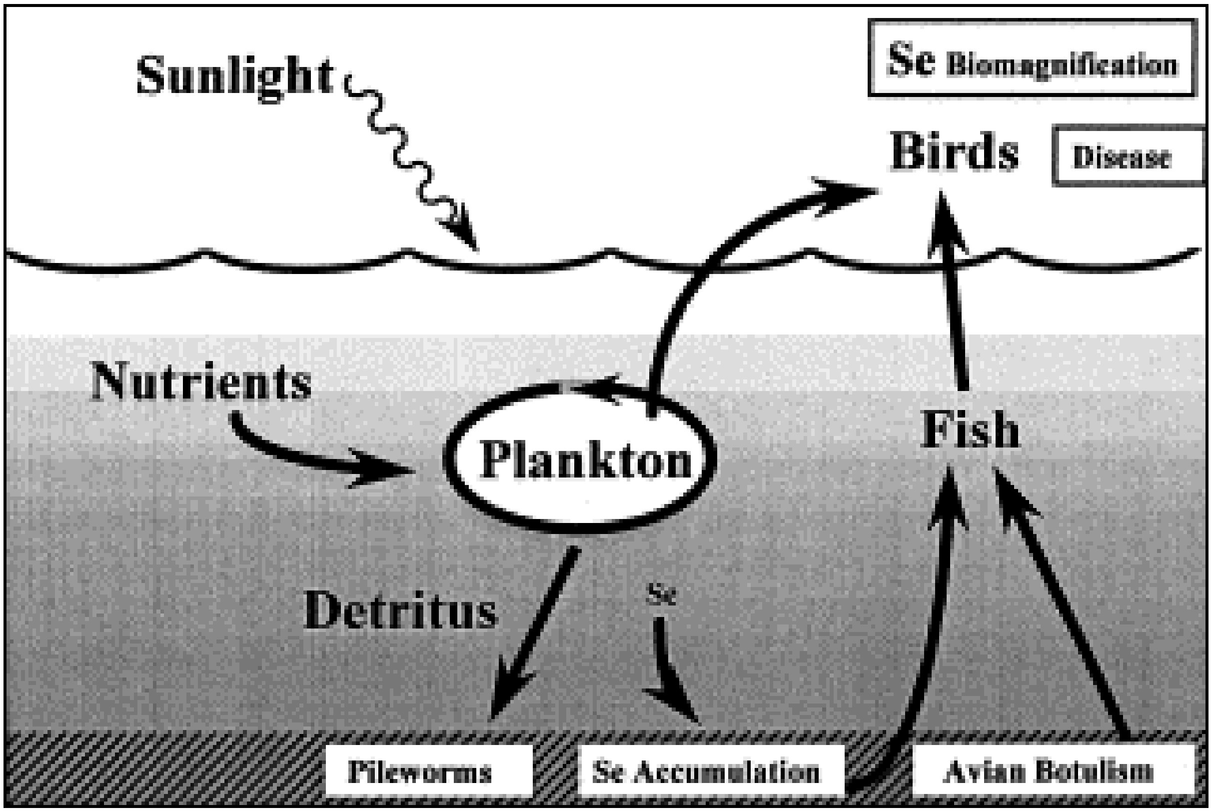

Figure 1. Schematic of the food chain showing pathways by which selenium and diseases are transmitted to birds in the Salton Sea.

In the beginning of the 21st century, the Salton Sea Authority and the U.S. Bureau of Reclamation pioneered efforts to evaluate and develop an alternative for restoration of the Salton Sea. On January 2008, the Legislative Analyst's Office released the report *Restoring the Salton Sea* (U.S. Bureau of Reclamation, 2007), which provided a summary of Bureau of Reclamation's studies to determine a preferred alternative action for restoration of the Salton Sea ecosystem and the protection of wildlife dependent on that ecosystem. The Salton Sea Ecosystem Restoration Program was coordinating efforts between the Legislature, various federal, state, and local agencies, stakeholders, and the general public to implement restoration activities at the Salton Sea. However, due to cuts in the budget of the state of California, the preferred restoration plan has been placed on hold. In addition to economic issues, politics also plays an important factor in the implementation of the plan.

HUMAN HEALTH

Selenium is an essential nutrient for living organisms (Eisler, 2000; Klasing, 1998). The proposed appropriate and estimated safe daily intake of selenium for a healthy adult is

50-200 μg/day. When daily dietary intakes of selenium exceed the capacity of the human body to eliminate it (500 mg/day for adults), toxic effects can appear (USEPA, 1991). One of the most important biological functions of selenium in the human organism is its antioxidant effect functioning as cofactor for reduction of the antioxidant enzyme glutathione peroxidase (Chappuis & Poupon, 1991; Levander & Burk, 1994). In addition, selenium plays a role in the functioning of the thyroid gland by serving as a cofactor for the thyroid hormone deiodinases.

Relationships between the low concentration of selenium in the geographical area of Keshan in China and a pathology called Keshan disease (selenium deficiency resulting in cardiomyopathy) was discovered by a Chinese research group in 1979. The disease mainly affected children aged between two and ten years and premenopausal women living in the town of the mountainous region that had a very low selenium content in its cultivated soils, resulting in food production with very minimum concentrations of this element (Navarro-Alarcón & López-Martinez, 2000). Dietary intake on the Chinese population affected by Keshan disease was estimated to be only about 3 μg/day (Yang et al., 1987). Additionally, muscle problems, digestive alterations, cardiovascular disease and rheumatic disturbances are among other significant pathologies associated with selenium deficiency in humans (Neve, Henry, Peretz, & Mareschi, 1987; Ortuño, Ros, Periago, Martinez, & Lopez, 1996). Selenium supplementation can be beneficial for individuals overall, in regions where there are very low environmental selenium levels.

In contrast, if high amounts of selenium are taken exceeding the tolerable upper intake level of 400 μg/day, selenium poisoning can occur. Selenosis (term used for selenium poisoning) may be acute or chronic. The effects of acute selenium poisoning vary depending on the route of exposure. Acute inhalation exposure to selenium primarily results in respiratory effects with irritation of the mucous membranes in the nose and throat, producing coughing, nosebleeds, dyspnea (difficulty breathing), bronchial spasms, bronchitis, and chemical pneumonia. There may also be gastrointestinal effects including vomiting and nausea; cardiovascular effects; neurological effects such as headaches and malaise; and irritation of the eyes (Navarro-Alarcón & López-Martinez, 2000).
Acute oral exposure to selenium compounds results in pulmonary edema and lesions of the lung; cardiovascular effects such as tachycardia; gastrointestinal effects including nausea,

vomiting, diarrhea, and abdominal pain; effects on the liver; and neurological effects such as aches, irritability, chills, and tremors. Chronic (long-term) exposure to high levels of selenium in food and water results in discoloration of the skin, deformation and loss of nails, reversible loss of hair (baldness), excessive tooth decay and discoloration, a garlic odor to the breath, weakness, lack of mental alertness, and listlessness. Yang et al. (1987) estimated that Chinese people living in highly seleniferous regions, who exhibited signs of selenosis, had dietary intakes of selenium ranging from 3,200 to 6,690 µg/day.

Several studies have suggested other pathologies associated with selenium. Simonoff and Simonoff (1991) indicated that diabetes mellitus has been related to alteration in the homeostasis of certain elements such as selenium. Macpherson, Balint, and Bacso (1995) showed that a serum Se level of less than 55 µg/l has been previously associated with an enhanced risk of coronary heart disease.

For some time now, selenium has been related to the prevention of cardiovascular diseases. An inverse correlation between the incidence of coronary disease in human beings and animals, and environmental or blood Se levels has been found (Piquer, Pons, Serrulla, Martinez, & Greus, 1991; Simonoff & Simonoff, 1991; Levander & Burk, 1994; Navarro-Alarcón, López-Garcia de la Serrana, Pérez-Valero, & López-Martinez, 1999).

CHAPTER 3

METHODS

This chapter describes the study site and the experimental design used in this research.

STUDY SITE

The study was conducted in the Imperial constructed wetlands site shown in Figure 2 (Imperial wetlands), which is part of the New River Wetlands project located in Imperial Valley, California (32°52’30”N, 115°39’03”W). The Imperial wetlands site was constructed in 2000 and is located along the New River, in southern California, approximately thirteen miles north of the international boundary near Imperial, California. The Imperial wetlands site is comprised of approximately 9 ha of water surface area, in which 1.2 ha are vegetated with bulrushes (*Schoenoplectus californicus*), tamarisk (*Tamarix* spp.), and wild grasses, receiving approximately 11,000m^3 of agricultural drain water from the “Rice Drain 3” agricultural drain per day with a residence time of 18 days. The Imperial wetlands site is unlined allowing a portion of the inflow water to seep into the ground. Rainfall in the Imperial Valley is usually very low, at 9 cm/year, occurring predominantly from November through April, and temperatures average 13 ˚C in the winter and 32 ˚C in the summer. Over 100 bird species are found in this region (www.newriverwetlands.com).

MEASUREMENT OF SELENIUM VOLATILIZATION

Selenium volatilization was measured monthly in the Imperial wetlands site from May 2010 to October 2010. A single module chamber made of 6.6-mm thick Plexiglas with dimensions 0.71 m long, 0.71 m wide, and 0.76 m high was placed over wetland plants. The chamber enclosed an area of 0.5 m^2 and had an internal volume of 0.38 m^3. A detailed description of chamber design, calibration, and application was previously reported by Lin, Hansen, and Terry (1999). Volatile selenium in the air from the chamber was trapped using an alkaline peroxide trap solution (30% H_2O_2 and ~0.05 M NaOH) (ACS grade, Fisher

Figure 2. Aerial photograph of Imperial wetlands site (17.5 hectares) of the New River Wetlands Project in Imperial Valley, California.

Scientific). The solutions were contained in a series of two 500-ml gas-washing bottles, each containing 200 ml of the trap solution. The gas-washing bottles were connected to each other in series with Teflon tubing. The volatile Se produced inside the chamber was then captured by pulling air from the chamber through the series of gas-washing bottles solution with a vacuum pump at a flow rate of $0.43m^3$ h-1. Selenium volatilization measurements were conducted in the Imperial wetlands site for 24 h period. The solutions from two gas-washing bottles were collected and taken to the lab, where samples were acidified with hydrochloric acid and then analyzed for Se by ICP-MS.

TEMPERATURE CONTROL INSIDE CHAMBER

Temperature is one of the most important environmental factors that affect the rate of Se volatilization (Frankenberger & Karlson, 1994b). For every 10°C increase in the temperature, the vapor pressure of volatile Se rises threefold to fourfold (Karlson, Frankenberger, & Spencer, 1994), which might significantly affect the transfer of volatile Se inside the chamber. To minimize the effect of rising temperature inside the chamber during measurement of Se volatilization in the field, a sun canopy was placed above the ground to shade the chamber from direct sunlight (see Figure 3).

Figure 3. Sampling chamber setup in the Imperial wetlands.

SAMPLING ANALYSIS

Inductively coupled plasma-mass spectrometry (ICP-MS) was used to estimate organic compounds of selenium, specifically dimethylselenide (DMSe). ICP-MS in speciation analysis of both inorganic and organic compounds of selenium such as dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) has been discussed and reviewed extensively in the literature. For selenium speciation analysis, ICP-MS has several advantages over more traditional detectors, including simultaneous detection of multi-element and multi-isotope with greater sensitivity. Reagents and standards used for ICP-MS analysis of dimethyl selenide (DMSe) are the following: Pure dimethylselenide (DMSe) obtained from Alfa Aesar; trace metal grade nitric acid (Fisher Scientific) and trace metal grade hydrochloric acid (JT Baker). The ICP-MS instrument performance was verified with certified reference material, National Institute of standards and technology (NIST) 1640a (Trace elements in natural water) by calculating its recovery (%).

CHAPTER 4

RESULTS

This chapter describes the sampling efficiency of the chamber system and reviews the results of rates of selenium volatilization monitored during the months of May, June, July, September and October of 2010 in the Imperial wetlands.

RECOVERY EFFICIENCY RATE OF APPLIED DIMETHYL SELENIDE STANDARD IN CHAMBER

The sampling efficiency of the chamber system was tested using a standardized recovery test. The recovery experiment was conducted by injecting a dosage of 1µL DMSe standard solution into the chamber through a 2-mm diameter opening on the top cover, with an air-liquid-tight and zero dead-volume micro syringe. The collection chamber was checked for leaks so as to prevent the standard solution from escaping the interior of the chamber. The opening on the bottom of the chamber was covered with a Plexiglas sheet and sealed with silicone sealant. The inlet port of the chamber was sealed with a Plexiglas cover and air was pumped into the chamber through the outlet port to build up a positive pressure that was measured by a water manometer connected to the chamber. After a desired pressure was reached inside the chamber, the outlet port was sealed and a soap solution was applied to all joints. If bubbles were found, then silicone sealant was applied to seal leaks. The chamber was considered leak-free after the water level in the manometer remained unchanged for at least ten minutes.

The recovery rate was defined as the ratio (%) of the collected Se to the total amount of Se injected into the chamber. The recovery of 1 µL DMSe at a flow rate of 0.43 m^3 h^{-1} and sampling duration of 24 hours was determined to be 91%.

SIGNIFICANCE OF SE REMOVAL BY VOLATILIZATION IN THE IMPERIAL CONSTRUCTED WETLANDS

Rates of Se volatilization were monitored during the months of May, June, July, September and October of 2010 in the Imperial wetlands located in the city of Imperial, California. Measurements of Se volatilization were used to evaluate the selenium removal efficiency by these wetlands. In May 2010, Se volatilization measurement was conducted a single time on a vegetated site (saltmarsh bulrush). During all other months, Se volatilization measurements were conducted on vegetated and non-vegetated sites of the Imperial wetlands. The recorded rate of Se volatilization on a vegetated site was much higher in May than any other month measured in this study. The highest rate of Se volatilization attained on a vegetated site was 342.8 μg m^{-2} day^{-1}. In June, we attained a Se volatilization rate of 46 μg m^{-2} day^{-1} for a vegetated site. In July, September and October, rates for vegetated sites were substantially lower, i.e. less than 3.2 μg m^{-2} day^{-1}. Previous studies showed that Se concentrations ranged from 2.7-5.4 μg/L in the inflow and from 2.0-4.8 μg/L in the outflow at the Imperial Wetlands (Johnson et al., 2009). The masses of Se removed from the inflow through biological volatilization by the Imperial wetlands for vegetated and non-vegetated sites were calculated using each rate measured during the months above-mentioned multiplied by the areas of the vegetated (12,000 m^2) and non-vegetated (90,000 m^2) sites respectively. To determine the importance of volatilization as a pathway of Se removal, the mass of Se volatilized daily during the months comprised in the study was calculated as a percentage of the mass of Se volatilized daily over the mass of Se input to the wetland daily (Table 1). The mass of Se input to the wetland daily was calculated using the mean inflow Se concentration of 3.602 μg/L multiplied by the daily inflow of 11,000 m^3.

Table 1. Se Volatilization Rates from Measurements Conducted in May, June, July, September, and October 2010 Using a 24-hour Sampling Duration, with Respective Percentage of Mass Se Removed from Inflow

Month	Vegetated Sites		Non-Vegetated Sites	
	Se (μg m^2 day^{-1})	% of Inflow	Se (μg m^2 day^{-1})	% of Inflow
May	342.8	10.40	NA	NA
June	46.0	1.40	7.0	1.60
July	3.2	0.10	1.1	0.30
September	2.1	0.06	0.4	0.10
October	0.9	0.03	0.2	0.04

To compare the levels of Se volatilization between vegetated and non-vegetated sites, a relative side by side comparison was made by averaging the rates of volatilization for vegetated and non-vegetated sites (Figure 4).

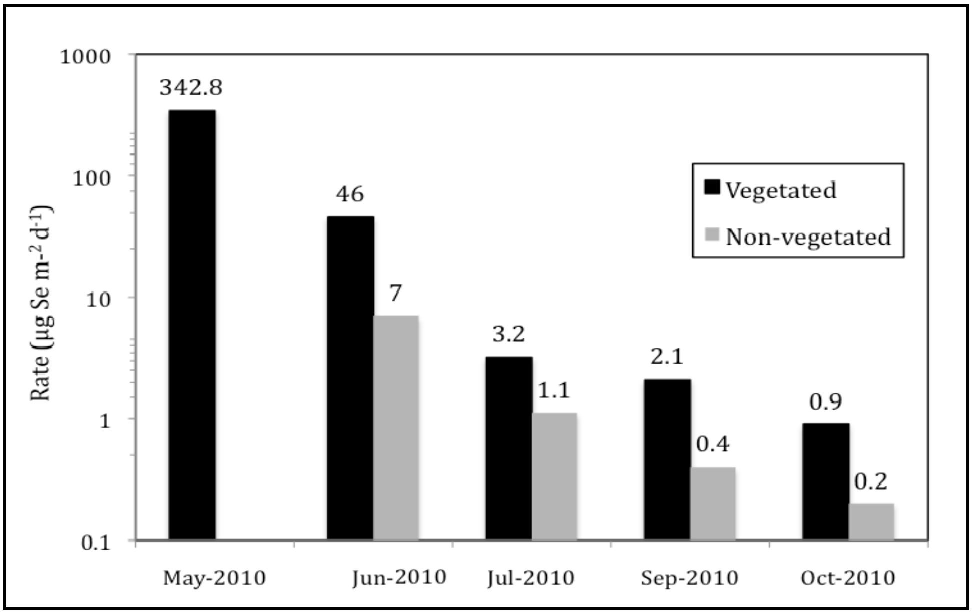

Figure 4. Rates of Se volatilization in the Imperial wetlands for vegetated and non-vegetated sites measured in 2010.

CHAPTER 5

DISCUSSION

The results of the volatilization measurements reported in this study show that Se volatilization rates are highly variable within the system, being relatively higher in May and June of 2010 and markedly lower in July, September and October of 2010 (Figure 4). Field measurements taken during the five months of 2010 showed that Se volatilization and respective percentage of mass Se removed from the inflow was always much higher in vegetated sites than non-vegetated sites (Table 1). For each of the direct measurement rates shown in Table 1, the overall respective percentage of selenium removed from the inflow by the Imperial constructed wetlands through biological volatilization was then calculated as previously described in the results section.

Se-collection chambers presumably collected volatile Se produced by both plants and microbes. The most dominant plant in the Imperial wetlands was bulrush. The mean rates of Se volatilization for this species varied substantially during the months of May, June, July, September and October of 2010: they were 342.8, 46.0, 3.2, 2.1 and 0.9 μg m^{-2} day^{-1} respectively.

Mean selenium mass removal efficiencies from the inflow at the Imperial wetlands for the five months study period were only 2.4% and 0.5% for vegetated and non-vegetated sites respectively. These volatilization losses were significantly lower than what was previously reported in a 1998 study at the San Francisco Bay wetland, where Hansen et al. conducted direct selenium field measurements. The values resulting from the San Francisco Bay study suggested that up to 10–30% of the total Se mass removed from the Chevron wetlands could have been volatilized. Weres, Jaouni, and Tsao (1989) also measured rates of Se volatilization in situ at the Kesterson Reservoir for vegetated and non-vegetated sites using enclosures. Rates from vegetated sites ranged from 24–192 μg m^{-2} day^{-1} as compared to our rates (0.9–342.8 μg m^{-2} day^{-1}). In another study, Lin and Terry (2003) calculated that the mean of the Se input volatilized at the Corcoran constructed wetlands over a two-year period was about 9%.

Johnson et al. (2009) estimated by mass balance calculation that approximately 17% of the selenium in the inflow of the Imperial constructed wetlands could have been lost through volatilization. The fact that our mean rates of selenium losses, directly measured by volatilization, were much lower in the same wetlands than Johnson et al. implies that these authors may have overestimated the contribution by volatilization to overall selenium losses in the Imperial constructed wetlands.

The lower rates of selenium volatilization we measured most likely resulted from many factors inherent in the Imperial wetlands, including: (1) the relatively low Se concentration present in the inflow, (2) the retention time in the wetlands, (3) the type of plant species (bulrush), (4) the high levels of sulfate in the sediments/soil, and (5) the absence of high levels of dissolved organic matter.

The selenium concentration coming on supplied irrigation water to the Imperial Valley has low selenium levels of approximately 2 μg /L (Setmire & Schroeder, 1998). Selenium can become concentrated through excessive irrigation and evaporation in the Imperial Valley, resulting in selenium concentrations in agricultural drain waters ranging from 6 to 28 μg /L, with an average concentration of 8 μg /L (Setmire & Schroeder, 1998). Our study utilized a mean selenium concentration of 3.602 μg /L (Johnson et al., 2009) for calculations of selenium removal efficiency in the Imperial constructed wetlands, which is a value below the water criterion of 5 μg /L established by the United States Environmental Protection Agency (USEPA, 2000). In contrast, the average Se concentration in the inflow observed in Lin and Terry (2003) studies conducted at the Corcoran constructed wetlands in California was 22 ± 2 μg $/L^{-1}$ in 1997, 21 ± 4 μg $/L^{-1}$ in 1998 and 16 ± 2 μg $/L^{-1}$ in 1999. Based on the Michaelis-Mentel kinectics model that describes the rates of irreversible enzymatic reactions by relating rate to the concentration of the substrate, it is expected that a wetlands system (i.e. Corcoran constructed wetlands, CA) containing higher concentrations of Se in the inflow, will show higher rates of Se volatilization than a system such as the Imperial constructed wetlands containing lower concentration of Se in the inflow.

Another important factor in selenium removal efficiency by a constructed wetland is retention time (Chow, Tanji, & Gao, 2004). Studies conducted by Lin and Terry (2003) reported a retention time of 7-21 days and mass removal efficiency of 69%, while studies conducted in the Imperial wetlands by Johnson et al. (2009) reported a retention time of 18 days and mass removal efficiency of 56%. The studies mentioned above did not measure volatilization directly as opposed to this study, which measured it directly and observed selenium removal efficiencies at the Imperial wetlands during the study period, using mean rates, of only 2.4% and 0.5% for vegetated and non-vegetated sites respectively. It is difficult to explain differences in selenium removal efficiencies based only on retention time. Other factors such as vegetation, microbial activity, and seasonal differences may also play important roles (Lin & Terry, 2003). Regions with colder climate may be more affected by seasonality. Lin and Terry (2003) showed through direct measurements of selenium volatilization that rates were up to 48% in the summer and less than 5% in the winter.

Vegetation is an important factor to Se volatilization not only because plants volatilize Se directly, but also because plants establish rhizosphere environments that support specific soil organisms that may significantly enhance Se volatilization (Azaizeh, Gowthaman, & Terry, 1997; Terry, Carlson, Raab, & Zayed, 1992). Our study showed (Table 1) that selenium volatilization rates measured from vegetated sites were approximately 190–557% higher than measurements from non-vegetated sites. Lin and Terry (2003) showed that rates of Se volatilization in different wetland cells vegetated with different plant species varies significantly. Selenium volatilization was highest in the rabbitfoot grass wetland cell, where 9.4% of the Se input was volatilized over a 2-year period. Selenium volatilization was lowest in the saltmarsh bulrush wetland cell, where only 0.6% of the Se input was volatilized over the same period. Bañuelos, Lin, Arroyo, and Terry (2005) observed relatively low rates of selenium volatilization from different plant species ranging from 14 to 39 $\mu g\ m^{-2}\ day^{-1}$, while our study observed rates of selenium volatilization from vegetated sites in the Imperial wetlands ranging from 0.9 to 346 $\mu g\ m^{-2}\ day^{-1}$. The four wetland cells of the Imperial wetlands have only 25% of its area vegetated with bulrushes (*Schoenoplectus californicus*), and therefore selenium volatilization rates might have been lower than other studies with more fully vegetated systems. Previous studies showed that volatilization could be enhanced in wetlands in many different ways, including the judicious use of plant species (Lin, Cervinka, Pickering, Zayed, & Terry, 2002; Terry et al., 1992).

The presence of sulfate in the sediments/soil is another important factor that may affect selenium volatilization rates. It is known that sulfate competes with selenate for uptake by the sulfate transporter as well as for the enzymes of the Se assimilation and volatilization pathway in plant tissues. Therefore, high levels of sulfate in soil can significantly inhibit selenate uptake and volatilization in most plant species (Zayed & Terry, 1994). Bañuelos et al. (2005) showed relatively low rates of selenium volatilization in vegetated agricultural drainage sediment from the San Luis Drain, Central California, due to high levels of sulfate. Sediment sulfate reduces a plant's ability to phytoextract and volatilize Se from the sediment (Zayed & Terry, 1994). Kadlec, Roy, Munson, Charlton, and Brownlie (2010) conducted sampling events for sulfate in the Imperial constructed wetlands, where a high sulfate content of 722 mg L^{-1} was observed in the drainage sediment (characteristic of regional circumstances). However, because of the high levels of sulfate in the drainage sediment, the extent to which Se can be removed via biological volatilization from agricultural drainage sediment has not been fully explored (Bañuelos et al., 2005).

Additionally, organic matter has been reported to be critically important for promoting microbial volatilization of Se (Frankenberger & Karlson, 1989). Higher rates of Se volatilization have been observed to occur when temperature, soil water content, and available organic carbon in soil were high (Bañuelos et al., 2005; Frankenberger & Karlson, 1994b; Lin & Terry, 2003). Earlier studies conducted by Frankenberger and Karlson (1989) showed that higher levels of Se volatilization can be achieved by amending seleniferous soils with different types of organic sources such as orange peels and protein mixtures, which help increase soil microbial activities associated with Se volatilization. In addition, the decomposition of organic matter generates methyl donors that enhance Se methylation process, ultimately increasing the production of volatile Se compounds of DMSe and DMDSe. The addition of available carbon from both methione and casein may also provide methyl groups for the methylation process that eventually contributes to the formation of DMSe in both vegetated and non-vegetated sites (Bañuelos & Lin, 2007; Zhang & Frankenberger, 1999). The low rates in Se volatilization observed in the Imperial constructed wetlands may have been partially due to the relatively low concentration of organic matter in the wetlands (i.e. BOD in the inflow 12 mg/L). It was, however, beyond the scope of this paper to identify how organic amendments may have influenced volatilization activity in vegetated and non-vegetated sites at the Imperial Constructed Wetlands.

CHAPTER 6

CONCLUSION

Results from this study support that conclusion that although Se volatilization occurs under naturally occurring field conditions in the Imperial constructed wetlands, it plays a relatively minor role in removing Se from agricultural wastewater. Results showed that Se volatilization in the Imperial wetlands occurs in both vegetated and non-vegetated sites and that Se volatilization rates were always higher at vegetated sites. Although, rates for vegetated and non-vegetated sites were not statistically different, rates of selenium volatilization from sites vegetated with bulrush plant species ranged from 0.2 to 342.8 $\mu g\ m^{-2}\ day^{-1}$, while rates of selenium volatilization from non-vegetated sites ranged from only 0.2 to 7.0 $\mu g\ m^{-2}\ day^{-1}$. Wetland management practices such manipulation of water levels, water chemistry, temperature, organic amendments and number and/or different species of plants may increase the efficiency of Se removal through biological volatilization. Further research is needed to fully understand the role of environmental factors on Se volatilization in the field and to enhance levels of Se volatilization though environmental manipulation.

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